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**NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D.C.**

25 May 1953
Report No. 700
(Special)
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**CHAIN-TRANSFER OF
NITRO COMPOUNDS IN
POLYMERIZATION REACTIONS**



**Contract N7onr-462
Task Order I**

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25 May 1953

Report No. 700
(Special)

THE CHAIN-TRANSFER OF
NITRO COMPOUNDS IN POLYMERIZATION REACTIONS

Contract N7onr-462

Task Order I

Written by:

T. R. Fukuto
J. P. Kispersky

Approved by:

DO NOT T.I.P.

K. Klager
K. Klager
Senior Organic Chemist
Solid Engine and
Chemical Division

No. of Pages: 39

M. H. Gold
M. H. Gold
Principal Chemist
Solid Engine and
Chemical Division

R. D. Geckler
R. D. Geckler
Senior Technical Specialist
Aerojet-General Corporation

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I. INTRODUCTION

A. This report is a summary of work which has been previously reported (Ref. 1).^{*} The work was undertaken to study the polymerization of 2,2,2-trinitroethyl methacrylate and to determine the chain-transfer constants of a number of aliphatic mononitro and polynitro compounds and a nitrate ester.

B. The use of a nitropolymer as a solid-monopropellant rocket fuel depends upon many factors. One of the most important is the ability of the rocket grain to resist deformation under stress so that it will retain its dimensions and thus avoid rupture (Ref. 1). It is known that the physical properties of an amorphous polymer are dependent upon molecular weight and that they approach a maximum limit with increasing chain length. However, the relationship is not linear, and below a certain critical molecular weight the magnitude of these properties rapidly falls to zero (Ref. 2). It is apparent, therefore, that only nitropolymers of high molecular weight, i.e., higher than the critical molecular weight, are of interest.

C. During work on the polymerization of 2,2,2-trinitroethyl methacrylate it was apparent that low-molecular-weight, friable polymers were being obtained. It was suggested that the nitro group was interfering with the normal polymerization reaction by terminating the chain radical, resulting in a polymer with a low degree of polymerization. Inasmuch as no data were available on the chain-transfer constants of aliphatic nitro compounds, a program was initiated to determine their transfer coefficients.

D. It is known that the chemical reactivity of a nitro group varies according to the structure of the molecule. Thus, primary and secondary nitro groups can form salts while tertiary nitro groups are unable to do so. Primary gem-dinitro groups activate the remaining hydrogen, and the resulting compound is quite acidic. However, gem-dinitro groups removed from the terminal position are quite resistant to base and are in general relatively inert. The trinitromethyl group under certain conditions (acidic) is relatively quite stable but under other conditions (basic) may be attacked quite rapidly. Therefore, the nitro compounds used as chain-transfer solvents were chosen to represent structures of differing chemical stability and those most likely to be found in a nitro vinyl monomer. These nitro compounds were used as transfer solvents in the polymerization of styrene, vinyl acetate, and methyl methacrylate because these monomers contain polarizable ethylenic double bonds to which are attached groups which differ in electronic character. As a further convenience, the polymerization characteristics of these monomers are well known, and equations for calculating degree of polymerization from intrinsic-viscosity measurements are given in the literature.

^{*}A list of references is presented at the end of this report.

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I Introduction (cont.)

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E. Flory (Ref. 16) was the first to recognize that in solution polymerization the activity of the growing polymer radical could be transferred to a solvent molecule, which was then capable of adding additional monomer units to form another polymer molecule. In the process the first polymeric radical ceased to grow further, and the overall result was isolation of a polymer with a lower degree of polymerization. Mayo (Ref. 17), studying the kinetics of styrene polymerization in various solvents, compared the efficiency of these solvents by relating polymer length to concentration of the monomer. Mayo also defined the chain-transfer constant. In the last ten years much work has been done in evaluating chain-transfer constants (Ref. 18, 19, 20). However, most of the work has been limited to the study of styrene or methyl methacrylate polymerization in the presence of mercaptans, hydrocarbons, or halogenated solvents. The only aliphatic nitro solvents which appear to have been used in polymerization reactions are nitromethane (Ref. 20, 21), 2-nitropropane (Ref. 22), and tetranitromethane (Ref. 23). In no case have chain-transfer constants been evaluated.

F. The only aliphatic nitromonomers which have been reported in the open literature are those containing only a single nitro group per molecule. These comprise the nitro olefins (Ref. 24, 25) and the nitroalkyl esters of acrylic, methacrylic, crotonic and maleic acids (Ref. 26 to 32). Most of these compounds, with the exception of the nitro olefins and the crotonates, appear to polymerize readily by a free-radical mechanism. 2-Nitroethyl acrylate and methacrylate (Ref. 33) and the mononitrostyrenes (Ref. 34, 35, 36) are also polymerized by free-radical initiators.

G. The scarcity of data in the literature referred to above does not permit a complete evaluation of the molecular weights of the polymers obtained. However, it appears that only the nitrostyrenes gave products of very low molecular weight.

H. This fact leads to the belief that the chain-transfer constant for aliphatic mononitro compounds is low. Inasmuch as no data were available for polynitro aliphatic compounds, it was decided to determine their reactivity toward free radicals by obtaining their chain-transfer coefficients. It is well known that polynitro aromatic compounds are inhibitors of free-radical polymerization (Ref. 37).

II. SUMMARY

A. The chain transfer constants for 12 aliphatic nitro compounds and a nitrate ester with methyl methacrylate were found to vary from $<10^{-4}$ to 1. Several possible mechanisms for the transfer reaction are discussed, along with attempts to substantiate the transfer by alpha-hydrogen abstraction by synthetic means.

B. The inhibition of methyl methacrylate polymerization is reported. The reason for the inhibition is believed to be the formation of $\text{NO}_2\cdot$ by scission of the carbon-nitrogen bond in tetranitromethane.

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II Summary (cont.)

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C. Attempts to determine the chain-transfer constants of the nitro compounds with styrene and vinyl acetate were unsuccessful because these compounds inhibited polymerization.

D. The polymerization of 2,2,2-trinitroethyl methacrylate using various initiator concentrations gave a polymer with a constant molecular weight, corresponding to a \bar{P}_n of about 12. The square of the rate was found to be proportional to the initiator concentration.

III. CONCLUSIONS

A. Inasmuch as the chain-transfer constants for trinitromethyl compounds reported in Table II are comparable with those which have been reported for mercaptans, it is obvious that monomers containing the trinitromethyl group will not give high-molecular-weight polymers. The loss of the high-energy trinitromethyl group in the future preparation of vinyl nitromonomers is disappointing. It will be difficult to replace this moiety by a suitable structure which can be easily synthesized and yet will contain sufficient energy to give a propellant of high specific impulse. It again becomes the task of the synthetic organic chemist to develop new methods for the preparation of other high-energy groupings.

B. The observed inhibition by aliphatic nitro compounds of vinyl monomers containing electron-donating groups (such as styrene and vinyl acetate) attached to the double bond, although unexpected, is a fact. It is therefore evident that all present effort directed toward the preparation of high-molecular-weight polymers from compounds such as nitrostyrenes or nitro vinyl esters is in vain. On the basis of this evidence, it is recommended that all such work now be discontinued. Past experience with vinyl esters of nitroacids also bears out this conclusion. Attempts to polymerize vinyl 4,4,4-trinitro-butyrate and vinyl 4,4-dinitrovalerate alone or to co-polymerize them with styrene, vinyl acetate, and acrylonitrile were unsuccessful. In the attempted co-polymerizations it was found that these nitromonomers inhibited the self-polymerization of styrene and vinyl acetate but not that of acrylonitrile. One negatively substituted nitro compound which failed to polymerize was methyl α (2,2-dinitropropyl) acrylate. The inability of this monomer to polymerize is probably due to the bulkiness of the dinitropropyl group. The failure of methyl α (tert-butyl) acrylate to polymerize has been pointed out as a case of steric hindrance (Ref. 47). It is believed that this nitro acrylate is also an example of steric inhibition.

C. Only the nitramino, nitrate, and isolated mononitro groups with chain-transfer constants of approximately 10^{-4} appear suitable for incorporation in a monomer from which one may obtain a polymer of reasonably high molecular weight.

D. The utility of secondary gem-dinitro groups cannot be accurately assessed. From the chain-transfer constant, chain lengths of approximately

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III Conclusions, D (cont.)

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1000 units should be possible. It is questionable whether such monomers would be of sufficient energy to function as monopropellants, but the field appears worthy of investigation.

IV. EXPERIMENTAL

A. POLYMERIZATION

1. In order to determine the chain-transfer constant of a solvent it is necessary to know the degree of polymerization of the polymers produced from a given monomer at several concentrations in the solvent. One must therefore know the solvent-to-monomer ratio and the degree of polymerization of the polymer. The degree of polymerization is calculated from the intrinsic viscosity using the equation $[\eta] = kM^a$, where k and a are constants characteristic of a particular monomer. By plotting the reciprocal of the degree of polymerization against the solvent-to-monomer ratio the chain-transfer constant may be found by determining the slope of the straight line produced. This relationship is given in Equation (13).

2. The chain-transfer polymerizations were conducted in 18 x 160-mm Pyrex test tubes which had been thoroughly cleaned in dichromate cleaning solution. In general, 10-ml aliquots of a 100-ml sample, prepared at 20°C, containing monomer, initiator, and transfer solvent, were placed in each test tube. The tube was then purged with nitrogen which had been freed of oxygen by bubbling it through a chromous chloride solution and dried by passing it through concentrated sulfuric acid. In some of these experiments the tubes were closed by sealing the glass tube, and in the remaining experiments the tubes were sealed with tight-fitting rubber stoppers enclosed in a thin polyethylene film. No difference in behavior was observed as the result of these procedures. The sealed tubes containing the monomeric mixture were then placed in a $45 \pm 0.1^\circ\text{C}$ water bath and removed at intervals. Upon removal, the tube was immediately cooled in dry ice and the polymer was precipitated by pouring the solution into 100 ml of methanol. The fibrous polymer obtained was collected on a coarse, sintered-glass funnel and dried over phosphorus pentoxide at a pressure of less than 1 mm. The weight of the polymer sample was then determined.

3. The bulk polymerization of 2,2,2-trinitroethyl methacrylate was carried out in cleaned 16 x 160-mm Pyrex test tubes, at $50 \pm 0.1^\circ\text{C}$. The required quantities of monomer and initiator were weighed, and the mixture was heated to 30°C to melt the monomer. Seven aliquots corresponding to five-gram samples were used in determining the rate of polymerization. Upon removal from the bath, the polymer was precipitated by pouring the mixture into 100 ml of n-hexane. The polymer was dried in vacuo over calcium chloride.

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IV Experimental (cont.)

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B. VISCOSITY DETERMINATIONS

1. In order to maintain essentially constant solvent and monomer concentrations, viscosity determinations were run on polymer isolated at 3% conversion. The relative viscosities of polymethyl methacrylate samples in chloroform solution were determined in a No. 50 Ostwald-Cannon-Fenske viscometer at 25°C, using a polymer concentration of 0.4 g/100 ml. For samples exhibiting very low molecular weights the relative viscosity was again determined at a higher concentration, provided that sufficient sample was available. The efflux time for chloroform alone was 76.5 sec, and varied between 85 and 325 sec for the polymer solutions. No kinetic-energy corrections were made.

2. The intrinsic viscosity, $[\eta]$, was calculated from a single determination, using the Baker-Philippoff equation

$$[\eta] = 8/c (\eta_r^{1/8} - 1)$$

where c is the concentration of the polymer solution g/100 ml, and η_r is the relative viscosity. Lindsley (Ref. 3) has shown that this equation represents the data most satisfactorily for nitrocellulose in acetone. Further justification for the use of this equation has been obtained by plotting the ratio of the specific viscosity divided by the concentration against concentration for one of the polymer samples. The data obtained from a polymethyl methacrylate sample, in which trinitroethane was used as a transfer solvent, are given in Table I.

TABLE I

VARIATION OF THE INTRINSIC VISCOSITY (CALCULATED
FROM THE BAKER-PHILIPPOFF EQUATION) WITH CONCENTRATION

Concentration g/100 ml CHCl ₃	η_r	η_{sp}/c	$[\eta]$ from B-P Equation
0.100	1.030	0.300	0.304
0.200	1.064	0.320	0.312
0.400	1.131	0.328	0.310
0.700	1.236	0.337	0.306
1.00	1.353	0.353	0.306

Average 0.31

By extrapolation of the η_{sp}/c vs c curve to zero concentration, $[\eta]$ is found to be 0.32.

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IV Experimental, B (cont.)

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3. The number average degree of polymerization was calculated from the equation derived by Baysal and Tobolsky (Ref. 4) for unfractionated samples of polymethyl methacrylate:

$$[\eta] = 2.52 \times 10^{-3} \bar{P}_n^{0.80}$$

4. Viscosity determinations on polystyrene were run in the same viscometer, also at 25°C, using a benzene solution whose concentration was 0.40 g/100 ml. The "intrinsic viscosity" was calculated from the relationship:

$$\left[\frac{\ln \frac{t}{t_0}}{c} \right]_{c=0.4}$$

where t is the efflux time of the solution, t_0 is the efflux time of the solvent, and c is the concentration of the polymer solution, measured in g/100 ml of solution.

5. Because the molecular weight of the polytrinitroethyl methacrylate polymers is low, the relative viscosity was determined using an acetone solution at a concentration of 2 g/100 ml. The intrinsic viscosity was calculated from the Baker-Philipoff equation.

C. PURIFICATION OF MONOMERS

1. The three monomers which were commercially available were fractionally distilled under nitrogen in a 3-ft, vacuum-jacketed, silvered column, packed with glass helices. (For styrene, the bp is 63°C at 50 mm; for vinyl acetate, the bp is 73°C, and n_D^{25} is 1.3932; for methyl methacrylate, the bp is 34°C at 62 mm, and n_D^{25} is 1.4125.)

2. The 2,2,2-trinitroethyl methacrylate was prepared by esterification of 2,2,2-trinitroethanol and methacrylic acid in refluxing benzene, using concentrated sulfuric acid as a catalyst. The water was removed azeotropically in a Dean-Stark water separator. The crude monomer was taken up in *n*-hexane and decolorized with charcoal. Several recrystallizations from *n*-hexane gave a white crystalline solid, mp 28.3°C.

D. SOURCES OF OTHER COMPOUNDS

1. Methyl *n*-amyl ketone peroxide was purchased from the Lucidol Division of the Novadel-Agene Corp. and was used without further purification.

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IV Experimental, D (cont.)

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2. 2,2-Azo-bis-isobutyronitrile was prepared by the method of Overberger, O'Shaughnessy, and Shalit (Ref. 5).

3. Tetranitromethane was prepared according to the method of Hantzsch and Rinckenberger (Ref. 6). It was further purified by steam distillation.

4. Nitroform was prepared from tetranitromethane by the procedure of Schimmelschmidt (Ref. 7).

5. Bromotrinitromethane was prepared by bromination of potassium nitroform (Ref. 8).

6. 2,2,2-Trinitroethyl propionate was synthesized by the method of Marans and Zelinski (Ref. 9); the mp was 23 to 24°C, and n_D^{25} was 1.4449.

7. 1,1,1-Trinitrobutane (bp 40°C at 1μ, n_D^{25} 1.4408) and 1,1,1-trinitroethane (mp 53 to 54°C) were prepared according to the method used at the University of Maryland (Ref. 10). It was necessary to purify the trinitroethane by sublimation at 30 to 35°C and 2.5 mm in order to separate it from "Compound 335."

8. 5,5,5-Trinitro-4,4-dimethyl-2-pentanone resulted from the addition of nitroform to mesityl oxide (Ref. 11); the bp was 80 to 90°C at 30μ, the mp was 19.5°C, and n_D^{25} was 1.4702.

9. 1,1,1-Trinitro-2-methyl-2-acetoxypropane was prepared by the method of Schenck and von der Forst (Ref. 12); the bp was 50 to 60°C at 30μ, the mp was 27.4°C, and n_D^{25} was 1.4476.

10. 1,1-Dinitropropane was obtained from the oxidative nitration of 1-nitropropane (Ref. 13).

11. 1-Nitropropane (bp 54.5 to 55.0°C at 45.7 mm, n_D^{25} 1.3991) and 2,2-dinitropropane (bp 54°C at 3 mm) were obtained from The Commercial Solvents Corp. and were distilled before use.

12. N-Nitropiperidine was prepared from N,N'-pentamethylene urea by the method of Franchimont and Klobbie (Ref. 14); the bp was 74°C at 1 mm, and n_D^{25} was 1.4958.

13. 1-Nitraminobutane was prepared according to the procedure of Van Erp (Ref. 15); the bp was 78°C at 1 mm, and n_D^{25} was 1.4929.

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IV Experimental, D (cont.)

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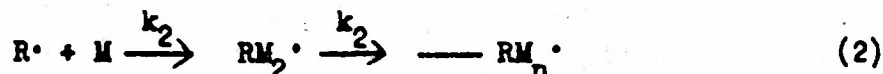
14. Ethyl nitrate was purchased from Eastman Organic Chemicals and was distilled before using; the bp was 84 to 85°C, and n_D^{25} was 1.3820.

V. THEORETICAL

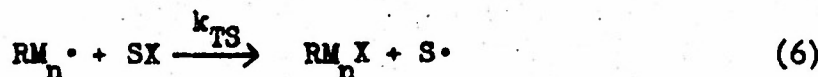
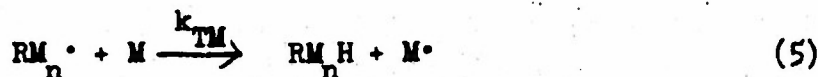
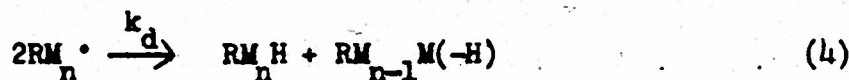
A. Although various authors have presented quite thorough kinetic studies of polymerization reactions in bulk and in solution, a brief summary would be advantageous here. The known facts of catalyzed polymerization are consistent with the following mechanism (Ref. 38):



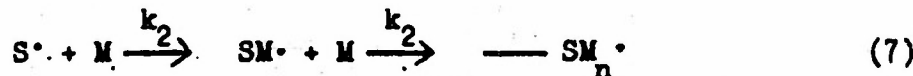
The reaction of the initiator radical R^\cdot with monomer M and successive additions of monomer gives the propagation step:



The polymer radical RM_n^\cdot is then terminated by one of the following reactions:



The active solvent radical S^\cdot then reacts with additional monomer M , forming another polymer radical:



This radical may also terminate by one of the above mechanisms.

B. In the present treatment, it is considered that the transfer to nitro solvent is large in comparison with the transfer to monomer; hence, the reaction represented by Equation (5) will be neglected.

C. The chain length V is equal to the ratio of the velocity of propagation to that of termination, i.e.

$$V = \frac{\text{velocity of propagation}}{\text{velocity of termination}} = \frac{\bar{P}}{n} \quad (8)$$

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V Theoretical, G (cont.)

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Substitution of appropriate values into Equation (8) gives

$$\bar{P}_n = \frac{k_2 C^* [M]}{(k_c + k_d) C^{*2} + k_{TS} C^* [SX]} \quad (9)$$

where C^* is the concentration of all active radicals and \bar{P}_n is the number average degree of polymerization. Assuming a steady-state concentration of radicals and no transfer to catalyst the following equations are obtained by substituting the value of C^* into Equation (9), and inverting:

$$k_1 [\text{Catalyst}] = (k_c + k_d) C^{*2}$$

$$C^* = \left(\frac{k_1}{k_3} [\text{Catalyst}] \right)^{1/2} \quad \text{where } k_3 = k_c + k_d \quad (10)$$

$$\frac{1}{\bar{P}_n} = \frac{(k_1 k_3 [\text{Cat}])^{1/2}}{k_2 [M]} + \frac{k_{TS} [SX]}{k_2 [M]} \quad (11)$$

D. In the absence of a solvent, the value of $1/\bar{P}_{n_0}$ in bulk polymerization is given by

$$1/\bar{P}_{n_0} = \frac{(k_1 k_3 [\text{Cat}])^{1/2}}{k_2 [M]} \quad (12)$$

Substitution of (12) in (11) gives

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n_0}} + C \frac{[SX]}{[M]} \quad (13)$$

where C has been defined by Mayo (Ref. 17) as the chain-transfer constant.

VI. DISCUSSION OF RESULTS

A. METHYL METHACRYLATE

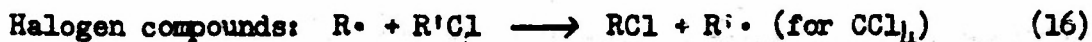
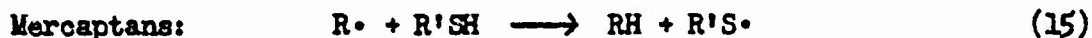
1. During the past ten years, a large amount of data on chain transfer during polymerization reactions has been accumulated. The classes of

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compounds which have been most often studied are hydrocarbons, mercaptans, and halogenated hydrocarbons. Little is known of the transfer of such solvents as esters, ketones, acids, and alcohols. There has been no study of aliphatic nitro compounds.

2. It has been ably demonstrated that the polymers formed in the presence of solvents containing halogen or sulfur contain these elements as an integral part of the polymer chain. There has been no conclusive evidence that hydrocarbon solvents are incorporated in the chain, but it can hardly be doubted that such is the case. The lack of evidence probably emphasizes the difficulty in detecting such groups, which form a very minor part of the polymer chain.

3. The mechanisms which have been postulated for the transfer of these solvents are the following:



The influence of the structure of R' upon the reaction with a polymer radical $R\cdot$ has been studied and is in accord with reactivities which have been observed from known organic reactions. The mechanism of transfer of nitro solvents seems to be more complex.

4. That aliphatic polynitro compounds are excellent chain-transfer agents is shown in Table II, which summarizes the solvent-to-monomer ratio $(SX)/(M)$, percent polymerization, intrinsic viscosity $[\eta]$, degree of polymerization \bar{P}_n , $1/\bar{P}_n$, and the chain-transfer constant C , for thirteen nitro compounds and a nitrate ester used as solvents in the polymerization of methyl methacrylate at 45°C with 0.25 mole percent of methyl *n*-amyl ketone peroxide. The chain-transfer constants were evaluated by the method given in the previous paragraph.

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VI Discussion of Results, A (cont.)

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TABLE II

CHAIN-TRANSFER CONSTANTS FOR METHYL METHACRYLATE
POLYMERIZATION IN VARIOUS SOLVENTS AT 45°C

Solvent	$(SX)/(M) \times 10^3$	% Polymer	$[\eta]$	\bar{P}_n	$1/\bar{P}_n \times 10^4$	C
None	0	3.56	3.05	7140	1.40	—
Tetranitromethane		Inhibits polymerization				
Nitroform	4.29	2.49	0.258	348	28.7	0.64
	8.44	2.48	0.180	209	47.9	0.55
	16.3	2.56	0.132	142	70.5	0.42
					Average	0.54
Bromonitroform	1.11	3.05	0.464	680	14.7	1.20
	2.48	3.08	0.274	350	28.6	1.10
	4.96	3.33	0.205	244	41.0	0.80
					Average	1.00
1,1,1-Trinitrobutane	3.49	2.70	0.230	282	35.5	0.98
	6.12	2.72	0.192	225	44.5	0.72
	11.5	2.93	0.108	110	90.9	0.78
					Average	0.83
2,2,2-Trinitroethyl Propionate	2.38	3.34	0.662	1059	9.45	0.34
	4.81	2.91	0.422	584	17.1	0.33
	10.4	3.15	0.254	325	30.8	0.28
	29.7	3.30	0.136	142	70.4	0.23
					Average	0.30
1,1,1-Trinitroethane	2.71	3.28	1.032	1850	5.40	0.15
	4.18	3.37	0.800	1330	7.52	0.15
	6.53	2.89	0.588	910	11.0	0.15
	8.48	2.85	0.510	766	13.1	0.14
	16.9	2.92	0.320	426	23.5	0.13
	36.1	2.33	0.180	208	48.1	0.13
					Average	0.14
1,1,1-Trinitro-2-methyl-2-acetoxypropane	9.31	3.66	0.929	1620	6.17	0.052
	23.7	2.59	0.508	760	13.2	0.051
					Average	0.052
5,5,5-Trinitro-4,4-dimethyl-2-pentanone	9.45	3.45	0.872	1490	6.71	0.056
	22.2	3.08	0.688	1100	9.06	0.035
	46.8	2.46	0.460	670	14.9	0.029
					Average	0.040

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VI Discussion of Results, A (cont.)

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TABLE II (cont.)

CHAIN-TRANSFER CONSTANTS FOR METHYL METHACRYLATE
POLYMERIZATION IN VARIOUS SOLVENTS AT 45°C

Solvent	(SX)/(M) x 10 ³	% Polymer	[η]	\bar{P}_n	1/ \bar{P}_n x 10 ⁴	C
1,1-Dinitropropane	19.6	2.66	1.70	3440	2.91	0.0077
	34.8	2.85	1.37	2630	3.80	0.0069
	64.2	2.44	1.00	1770	5.65	0.0066
	87.6	3.03	0.863	1500	6.66	0.0060
					Average	0.0068
2,2-Dinitropropane	19.6	3.10	2.59	5810	1.72	0.0016
	52.1	2.43	2.10	4470	2.24	0.0016
	189	2.57	1.32	2500	4.00	0.0014
					Average	0.0015
1-Nitropropane	66.9	2.91	2.35	5160	1.94	0.00081
	221	3.23	2.08	4420	2.26	0.00038
	347	4.19	1.73	3510	2.85	0.00042
					Average	0.00050
N-Nitropiperidine	19.1	3.36	3.20	7580	1.32	0
	39.7	2.79	3.24	7700	1.30	0
	122	2.89	1.95	4110	2.43	0.00082
					Average	?
1-Nitraminobutane	99.6	2.52	3.91	9700	1.03	0
	224	0.836	3.79	9400	1.06	0
	580	3.03	4.12	10,400	0.96	0
					Average	0
Ethyl Nitrate	30.1	3.90	2.91	6730	1.49	0.00030
	73.3	4.02	2.93	6790	1.47	0.000096
	255	3.97	2.49	5540	1.81	0.00020
					Average	0.00020

5. Comparing the chain-transfer constants given in the last column of Table I, it is apparent that as the number of nitro groups in a compound increases the chain-transfer reactivity increases. The large numerical value of most of the transfer constants shows that polynitro compounds are efficient transfer agents. It is of interest to compare these solvents with mercaptans. For methyl methacrylate and *n*-butyl mercaptan at 60°C, Walling (Ref. 39) reported a value of C equal to 0.67. For the same monomer and *n*-amyl mercaptan at 100°C, Smith (Ref. 40) found a C value of 0.8.

6. Of the nitro compounds studied, only tetranitromethane may be classed as an inhibitor. The conversion curves (Figure 1) obtained for several concentrations of nitro compound are similar to those obtained by Foord with styrene and *p*-benzoquinone at 90°C (Ref. 41).

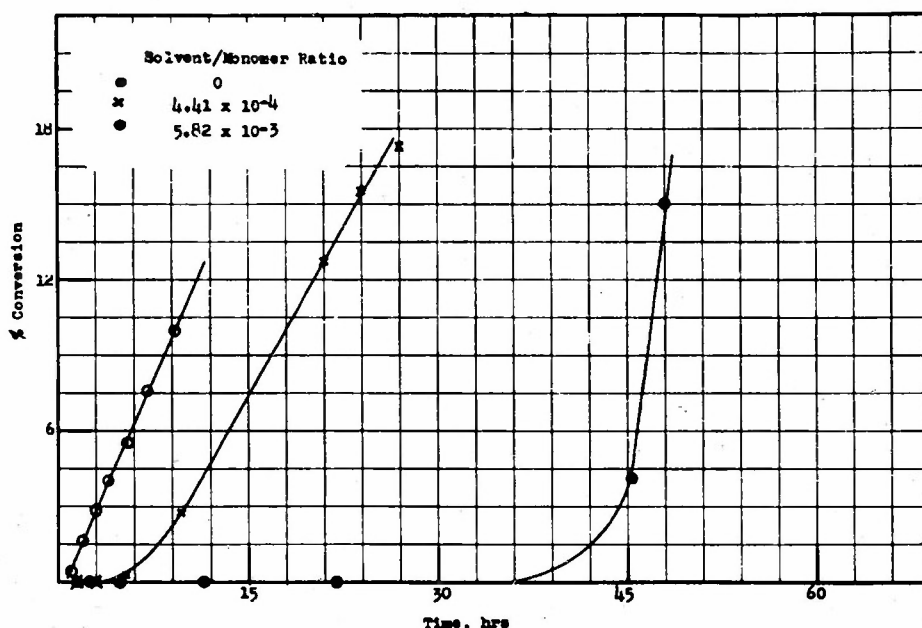


Figure 1

Rate of Polymerization of Methyl Methacrylate
in the Presence of Tetranitromethane

7. The transfer constants are so large that the question arises as to which reaction is responsible for the great reactivity of these compounds. Examination of the data in Table II yields the following facts: First, all of the nitro solvents (with, of course, the exception of tetranitromethane) can be classed into four broad groups, according to the magnitude of the transfer constant; second, each group differs from the succeeding one in that the average transfer constant for the group differs by a factor of approximately 10 from the average transfer constant for the succeeding group; third, nitramino groups, within the probable limit of error, do not transfer readily. The groups are listed in Table III.

TABLE III

NITRO COMPOUNDS IN ORDER OF DECREASING CHAIN-TRANSFER CONSTANTS

Compound	C		Group Average
Bromonitroform	1.0		
1,1,1-Trinitrobutane	0.83		
Nitroform	0.54	Group 1	0.56
2,2,2-Trinitroethyl propionate	0.30		
1,1,1-Trinitroethane	0.14		

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VI Discussion of Results, A (cont.)

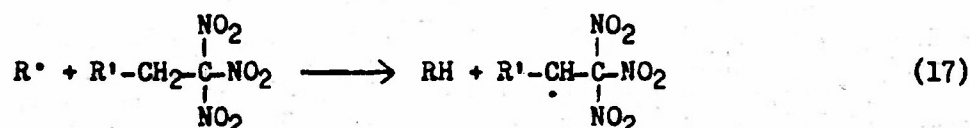
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TABLE III (cont.)

NITRO COMPOUNDS IN ORDER OF DECREASING CHAIN-TRANSFER CONSTANTS

<u>Compound</u>	<u>C</u>		<u>Group Average</u>
1,1,1-Trinitro-2-methyl-2-acetoxypropane	0.052	Group 2	0.046
5,5,5-Trinitro-4,4-dimethyl-2-pentanone	0.040		
1,1-Dinitropropane	0.0068	Group 3	0.0042
2,2-Dinitropropane	0.0015		
1-Nitropropane	0.00050	Group 4	0.00035
Ethyl nitrate	0.00020		

An explanation of the large difference in reactivity of the trinitromethyl compounds of Groups 1 and 2 now becomes necessary. Excluding nitroform and bromonitroform, it has been postulated that the reactivity of the compounds in Group 1 is due to the structure of the radical R' attached to the carbon atom which is alpha to the trinitromethyl group. It was assumed that the transfer reaction occurred by extraction of an alpha hydrogen; e.g.,



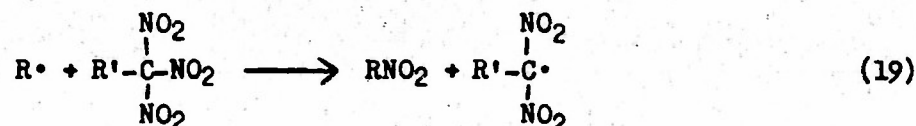
If this is true the reactivity of the radical R' follows the order



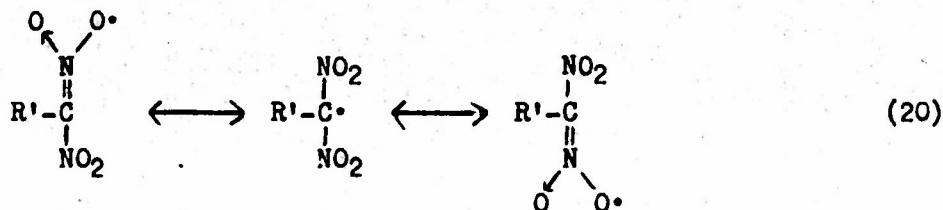
This is in accord with the order cited by Nozaki (Ref. 42) for stabilization of a substituted methyl free radical, R'CH₂•. Thus, it would be expected that a radical reacting with a series of compounds would react most readily with the compound which in turn gives a radical of greatest stability. It is unfortunate that the range of reactivity of the three radicals mentioned above is not very great. It would be interesting to try 1,1,1-trinitro-2-phenylethane as a transfer solvent because reaction with a polymeric radical would give a very stable transfer radical if hydrogen abstraction occurred. This stability would arise from the fact that four nearly equivalent resonance structures can be drawn for the free radical.

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8. In an attempt to verify this hypothesis, two compounds which contained no alpha hydrogen were synthesized. It was reasoned that if the mechanism postulated for the transfer reaction was correct these compounds would have very low chain-transfer constants. It can be seen from Table III that the average transfer constants for 1,1,1-trinitro-2-methyl-2-acetoxypropane and for 5,5,5-trinitro-4,4-dimethyl-2-pentanone are lower than those of Group 1 by a factor of nearly 10. The most important observation, however, is that the constants are still quite large. Thus, if the abstraction of alpha hydrogen were the only transfer reaction the reactivity of these compounds should approximate those of esters and ketones. However, their constants are approximately 500 to 2000 times larger than those observed for methyl ethyl ketone and ethyl acetate (Ref. 18). One is led to the conclusion that another reaction is occurring either simultaneously with or exclusive of the alpha-hydrogen reaction. The next most logical reaction seems to be transfer of a nitro group:



However, if this transfer occurs exclusively the reason for the difference of reactivity of the compounds listed in Group 1 is not apparent. One other argument against this mechanism is the fact that the nitro radical which is formed would have considerable resonance stability. This should give a transfer radical



which is unable to initiate another chain, and a decrease in polymerization rate would result. It is observed that, in general some retardation does occur. This is shown in Figures 2, 3, and 4, which show the conversion with time for the polymerization of methyl methacrylate in the presence of trinitrobutane, trinitroethyl propionate, and trinitrodimethylpentanone, respectively. However, trinitroethane and trinitromethyl acetoxypentane appear to cause an acceleration of the polymerization rate. This is shown in Figures 5 and 6.

9. Several attempts were made to prove the alpha-hydrogen reaction hypothesis by synthesizing simple compounds whose structure could be characterized. In one experiment 4,4,4-trinitrobutyric acid was permitted to react in concentrated refluxing benzene solution with 2,2'-azo-bis-isobutyronitrile

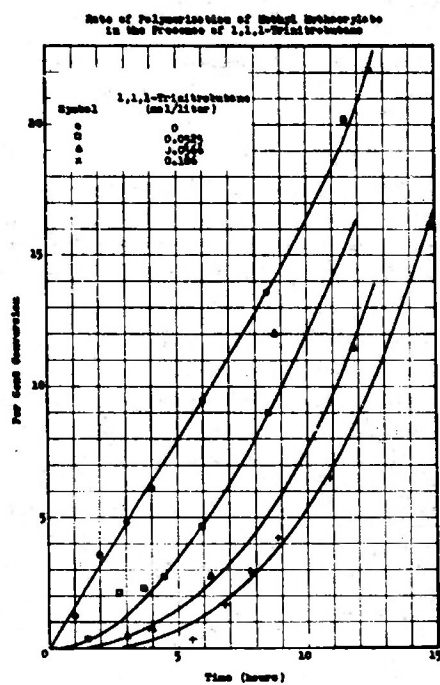


Figure 2

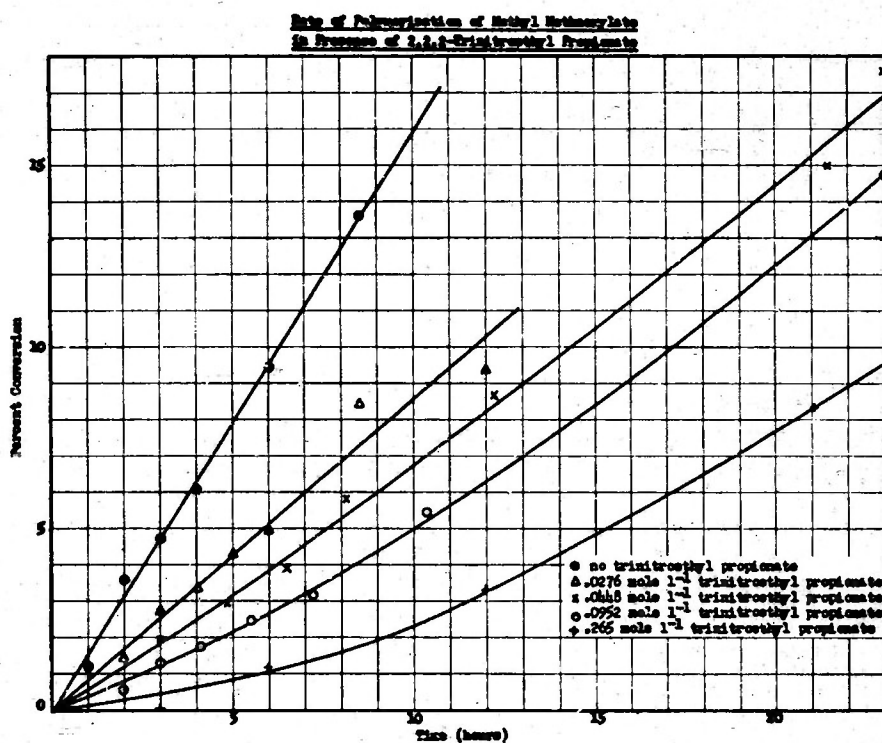


Figure 3

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VI Discussion of Results, A (cont.)

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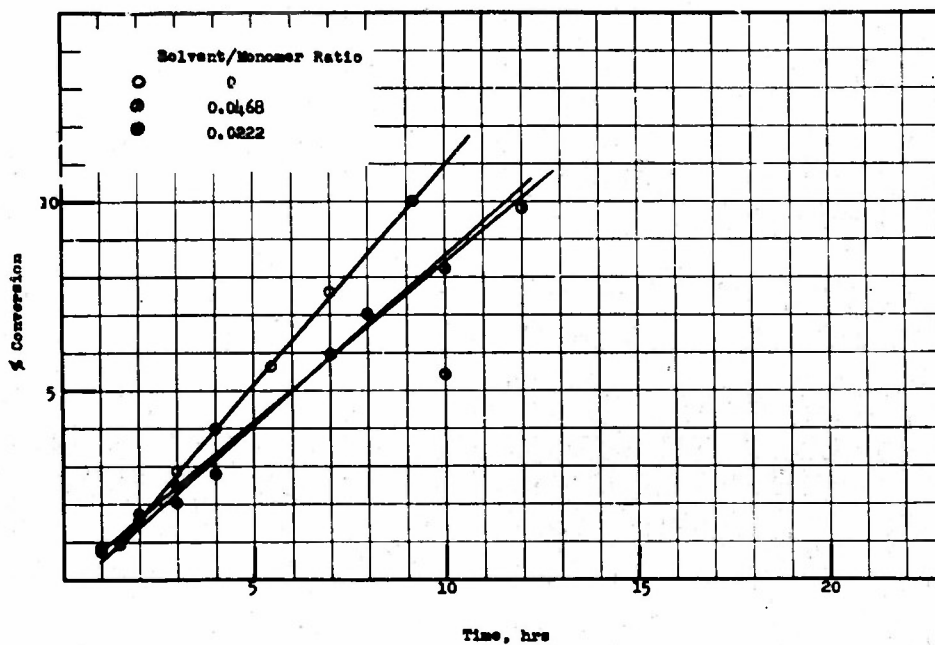


Figure 4

Rate of Polymerization of Methyl Methacrylate
in the Presence of 5,5,5-Trinitro-4,4-dimethyl-2-pentanone

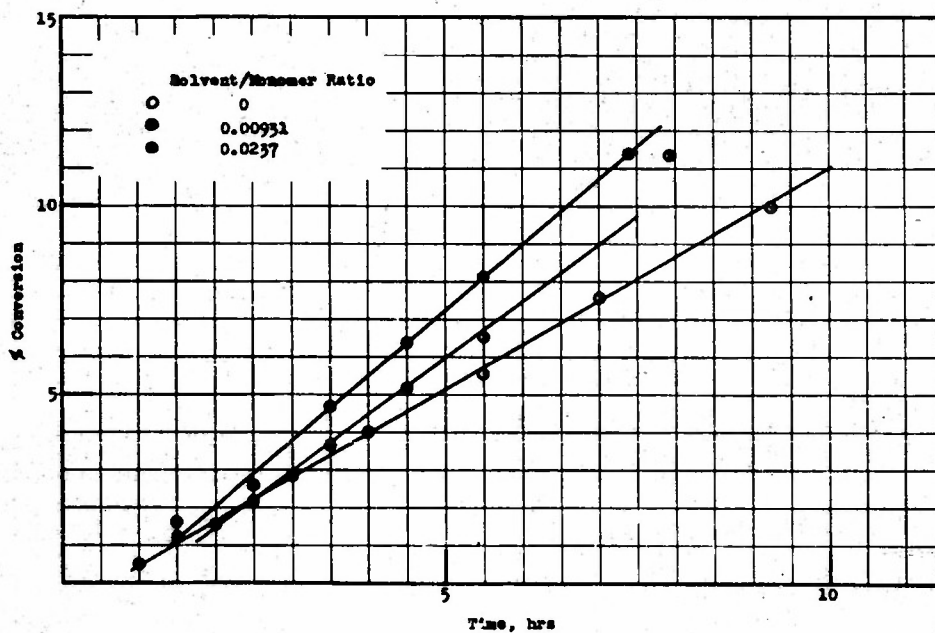


Figure 5

Rate of Polymerization of Methyl Methacrylate
in the Presence of 1,1,1-Trinitro-2-methyl-2-acetoxyp propane

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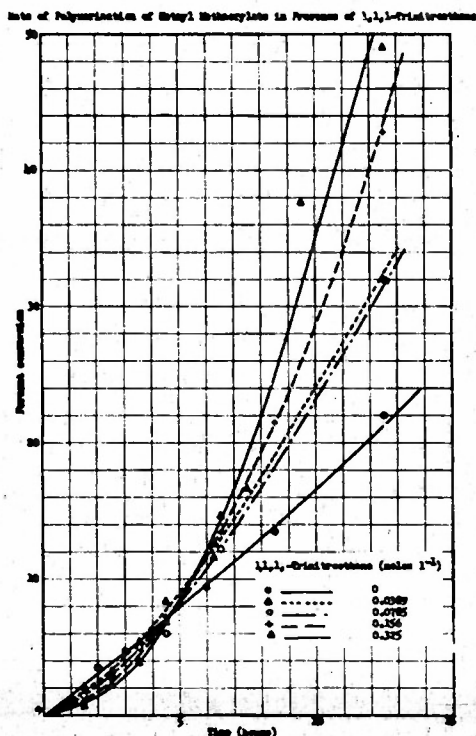


Figure 6

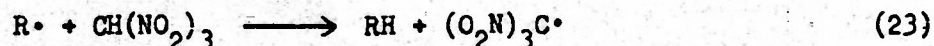
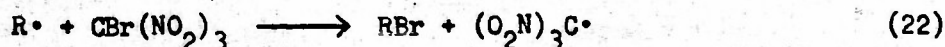
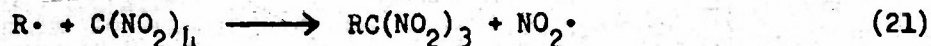
for 46 hr. It was observed that about 10 mole % of carbon dioxide was evolved, but no 3,4-di(trinitromethyl)-1,6-hexanedioic acid was found. The only acidic material isolated was the trinitrobutyric acid, which was recovered in 75% yield. 1,1,1-Trinitroethane was permitted to react with the azonitrile, using the same conditions, hoping to obtain 1,1,1,4,4,4-hexanitrobutane. However, the trinitroethane was recovered in 68% yield. The residue was a gummy, intractable material from which none of the desired product could be isolated. It is noteworthy that no 1,1-dinitroethane could be detected in the reaction products. Likewise, the addition of trinitroethane to cyclohexene, using free-radical catalysts, proved unsuccessful. It is possible that the use of another initiator producing a more reactive radical might have led to a successful reaction.

10. It must be concluded that the exact mechanism of the transfer reaction of trinitromethyl compounds remains unknown. It is even conceivable that two or more different reactions occur simultaneously. Which reaction predominates to give the observed transfer constant depends upon the structure of the compound in question.

11. It is not within the scope of the work on nitropolymers to determine transfer coefficients of non-nitro solvents, but it is apparent that an extremely fertile field lies in determining the reactivities of solvents containing active hydrogen, such as diethyl malonate, tricarbethoxymethane, phenylacetic ester and the like.

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12. The large chain-transfer constants observed for bromonitroform and nitroform are probably due to the ease of scission of the carbon-bromine and carbon-hydrogen bonds. The difference between the inhibitory action of tetranitromethane and the retarding influence of these compounds can be explained by assuming transfer of the trinitromethyl group; i.e.,



In the latter two cases the transfer radical might be reactive enough to initiate new chains, whereas the NO_2 radical is a known polymerization inhibitor (Ref. 43). Other pertinent information regarding this reaction may be obtained from the work performed at the University of Maryland (Ref. 44), where the addition of tetranitromethane to olefins and other unsaturated compounds was studied. The reaction of tetranitromethane with trimethylethylene, with or without added peroxide, yielded a yellow, viscous oil corresponding in composition to two molecules of olefin with one molecule of nitro compound. Methyl methacrylate and tetranitromethane gave an oily product containing three molecules of ester with one of nitro compound. Other unsaturated compounds which reacted with tetranitromethane were butadiene, cyclooctatetraene, quinone, isobutylene, allyl alcohol, cinnamyl alcohol, ethylene, vinyl acetate, and styrene. All except quinone and allyl alcohol reacted to give addition products corresponding roughly to two moles of unsaturated compound with one of nitro compound. The complete characterization of these addition products has not been carried out.

13. It may be concluded that tetranitromethane enters into the telomerization reaction in a manner similar to carbon tetrachloride. In the role of telogen the nitro compound definitely reacts by scission of the carbon-nitrogen bond. In the light of this information the inhibitory action of tetranitromethane as explained above appears logical.

14. Work carried out at the Evans Research and Development Corporation (Ref. 44) on the addition of chloro and bromonitroform to olefins, with added peroxide, indicated that polymeric material of unknown composition was obtained. The difference between the low-molecular-weight addition products of tetranitromethane and the polymeric materials obtained using the halonitroforms reflects the difference in the reactivity of the transfer radicals. The data on $1/P_n$ against solvent-to-monomer ratio for bromonitroform and nitroform are plotted in Figure 7. It is observed that curves are obtained, instead of the linear relationship indicated by Equation (13). In fact, many of the chain-transfer constants listed in the last column of Table II decrease slightly with increasing concentration. This indicates that some side reaction which has not been accounted for occurs along with the transfer reaction.

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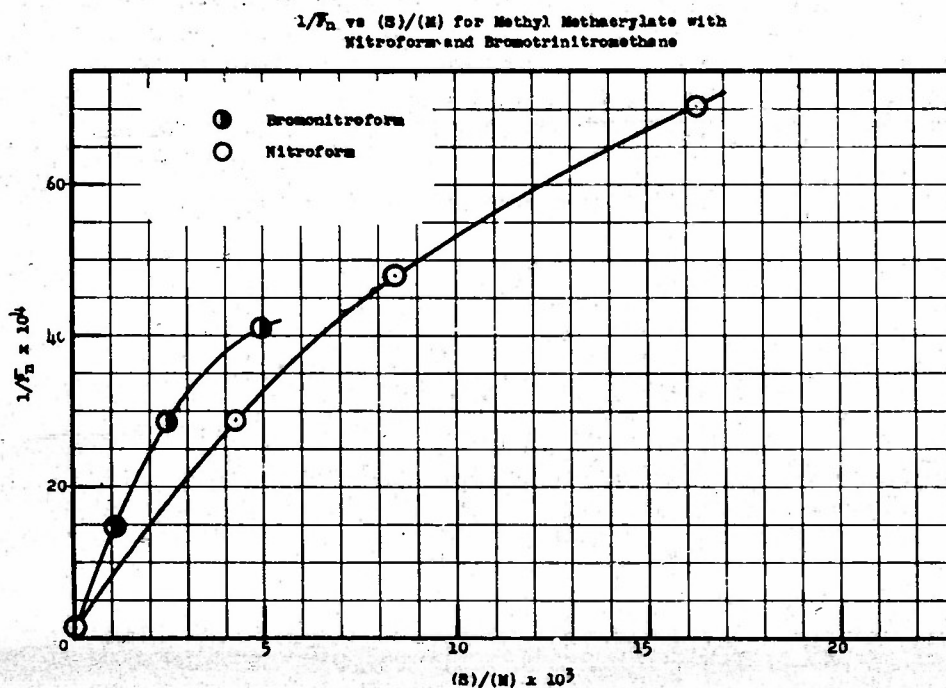
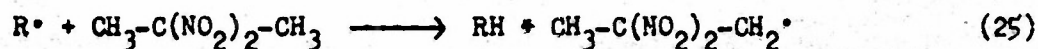
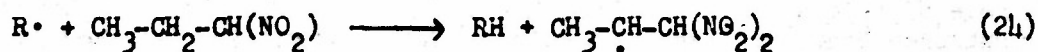


Figure 7

15. The difference in reactivity between 1,1-dinitropropane and 2,2-dinitropropane would also be accounted for by the alpha-hydrogen hypothesis. Inasmuch as 1,1-dinitropropane would give a secondary radical which would be more stable than the primary radical produced from 2,2-dinitropropane, it would be easier to form. These reactions are illustrated in the following equations:



It might also be postulated that the active hydrogen in 1,1-dinitropropane would contribute to its greater transfer reactivity. However, the nature of the transfer of 2,2-dinitropropane still must be accounted for, since both compounds are 150 to 700 times more reactive than aliphatic hydrocarbons.

16. The chain-transfer constants for 1-nitropropane and ethyl nitrate are low and nearly equal. These transfer constants are only about 20 to 50 times those observed for hydrocarbons. The true nature of the reaction is undoubtedly elucidated by the arguments already presented.

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VI Discussion of Results, A (cont.)

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17. The inactivity of 1-nitraminobutane in the transfer reaction, as compared with 1-nitropropane, might be due to the fact that the acidic hydrogen is more difficult to remove from the nitrogen atom because of its greater electro-negativity.

B. STYRENE

1. Attempts were made to obtain the chain-transfer constants of these nitro solvents with styrene. It was observed that polynitro compounds inhibit the polymerization of styrene very effectively. Only small molar quantities are needed to retard greatly or stop completely the formation of polymer. Table IV presents the data for the polymerization of styrene in the presence of 2,2,2-trinitroethyl propionate using 2 mole % of methyl *n*-amyl ketone peroxide as initiator. The percent polymerization was determined after 40 hr at 45°C.

TABLE IV
POLYMERIZATION OF STYRENE AT 45°C WITH VARIOUS
CONCENTRATIONS OF 2,2,2-TRINITROETHYL PROPIONATE

$(S)/(M) \times 10^3$	Approximate Mole % of Nitroester	% Polymer	$\left[\frac{\ln \eta_r}{c} \right]$ at $c=0.4$ g/100 ml
248	20	0	—
111	10	0	—
73.9	7	0	—
52.5	5	0	—
34.3	3	0	—
19.0	2	Trace	—
10.5	1	Trace	—
4.89	0.5	1.08	0.052
1.87	0.2	32.6	0.121
1.04	0.1	53.1	0.132
0.526	0.05	59.0	0.144
0	0	62.0	0.144

2. In a series of experiments using 0.22 mole % of catalyst and smaller quantities of the solvent, the retarding effect of the nitroester was illustrated. The rate of conversion is shown in Figure 8, using various quantities of solvent. The data given in Table V show the change of "intrinsic viscosity" of the polymer with conversion.

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Rate of Polymerization of Styrene
in presence of 2,2,2-Trinitroethyl Propionate

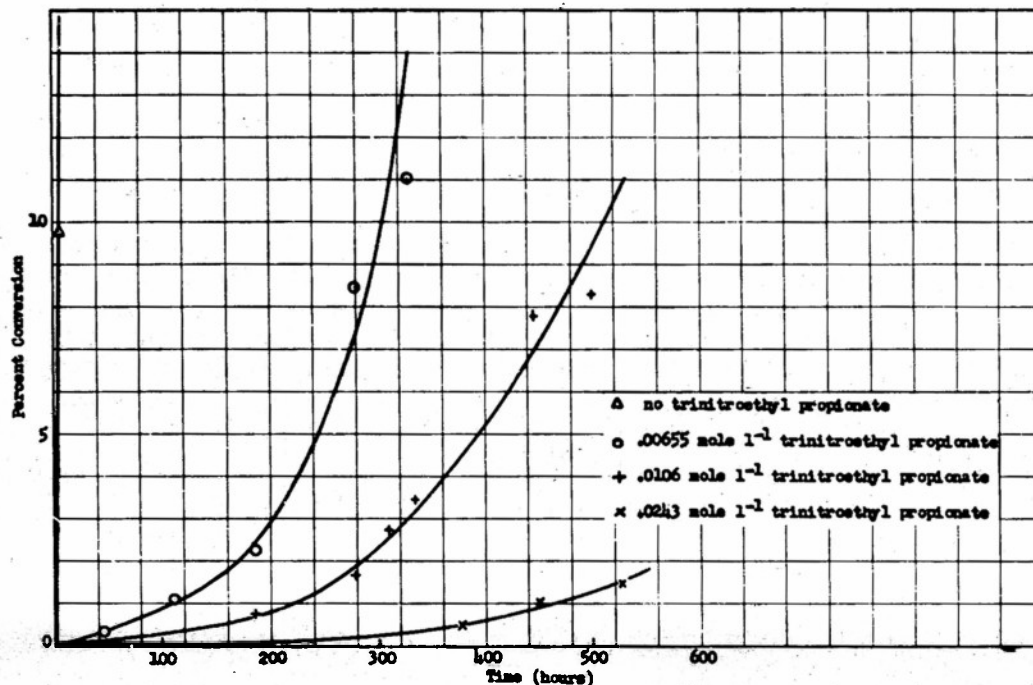


Figure 8

TABLE V

"INTRINSIC VISCOSITY" OF POLYSTYRENE SAMPLES

<u>Trinitroethyl Propionate</u> <u>moles/liter</u>	<u>Time</u> <u>hr</u>	<u>%</u> <u>Polymer</u>	<u>$\left[\frac{\ln \eta_r}{c} \right]$</u> <u>at $c=0.4$ g/100 ml</u>
0	5.8	9.72	0.341
0.00655	186	2.28	0.143
0.00655	279	8.45	0.359
0.00655	328	11.08	0.454
0.0106	334	3.44	0.202
0.0106	447	7.76	0.331
0.0106	495	8.82	0.331
0.0243	527	1.47	0.120
0.0533	546	0	—

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VI Discussion of Results, B (cont.)

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3. From the data of Figure 8, it is evident that trinitroethyl propionate concentrations as low as 0.00655 mole/liter retard the polymerization of styrene profoundly. In carrying out these experiments it was noted that the monomeric mixtures of Table IV containing 0.0106 mole/liter or less of nitro compound were colorless, whereas the other samples containing more solvent were deep yellow.

4. The inhibition reaction appears to be complex, since under certain conditions a crystalline substance of indefinite composition and unknown structure was isolated. The reaction of styrene, methyl *n*-amyl ketone peroxide, and trinitroethyl propionate was carried out in the following manner: A mixture containing 5.0 g of nitroester, 8.0 g of styrene, and 2.0 g of peroxide was sealed in a Pyrex test tube under nitrogen. After four days at 45°C a colorless, crystalline solid was isolated by cooling the mixture in dry ice. The products isolated from three such preparations gave the following analytical results:

Sample	mp, °C	%C	%H	%N
A	98 to 99	66.89	5.49	6.79
B	99.0 to 99.5	49.98	5.53	5.18
C	99 to 100	71.66	5.70	5.11

5. Sample B, which was isolated in greatest quantity and hence was most carefully purified, had a molecular weight of 248, determined cryoscopically in benzene. An infrared spectrogram of this sample showed the presence of a nitro group at 6.4 μ . There is some question whether this absorption in conjunction with the strong absorption in the region between 7.0 and 8.0 μ is due to a mono, *gem*-dinitro, or a trinitromethyl group. Strong absorption was found at 5.9 to 6.0 μ . This can be attributed to a carbonyl group which may be present in an ester, aldehyde, or ketone. Other absorptions were observed at 9.2 μ , 10.0 to 10.2 μ , and 11.4 μ . The absorption occurring at 10.0 to 10.2 μ could possibly be due to an aromatic ring. When benzene was substituted for styrene in these experiments, or the peroxide catalyst was omitted, none of the crystalline product was isolated. At present, it can only be said that this material contains one or more nitro groups, one or more carbonyl groups, and is possibly an aromatic compound. The fact that styrene is necessary for its production and that its composition may vary makes it seem likely that these substances are reaction products of the nitroester and several styrene units. Another fact that supports this reasoning is that the use of 2,2-azo-bis-isobutyronitrile in place of methyl *n*-amyl ketone peroxide gave similar results.

6. It is apparent that the use of styrene was unsuited for the determination of chain-transfer constants of these polynitro compounds. Therefore, no further work was carried out with this monomer.

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C. VINYL ACETATE

1. Vinyl acetate is much more sensitive to the inhibitory action of polynitro compounds than is styrene. For example, the bulk polymerization at 45°C of vinyl acetate containing 0.25 mole % peroxide catalyst gave a 16.7% conversion of monomer to polymer after 64 hr. However, the addition of 2,2,2-trinitroethyl propionate in an amount equal to or greater than the quantity of catalyst gave no polymer after 21 days. When only 0.1 mole % of nitro ester was present only 1.2% of polymer was obtained after 300 hr. In all experiments the samples, although initially colorless, turned yellow after several days in the 45°C bath. The intensity of the color seemed proportional to the initial concentration of trinitroethyl propionate and appeared to increase with time.

2. Similar experiments with 2,2-dinitropropane showed that it too is an effective inhibitor for the polymerization of vinyl acetate. The bulk polymerization of vinyl acetate containing 3.4 mole % of the dinitropropane, carried out using the same conditions mentioned in the previous paragraph, gave no polymer after 142 hr.

3. Inasmuch as the rate of polymerization in the presence of nitro compounds was too slow to be of convenience no further work was done with this monomer. No low-molecular-weight adduct was isolated, in contrast with the experiments using styrene.

D. 2,2,2-TRINITROETHYL METHACRYLATE

1. The above work clearly shows the effect of a solvent containing nitro groups upon the polymerization of a vinyl monomer. A vinyl monomer which contains nitro groups would therefore be expected to exhibit a self-modifying polymerization, producing polymers of constant chain length. This is true of trinitroethyl methacrylate. The high chain-transfer constant for the trinitromethyl group suggests the formation of a low-molecular-weight polymer with a degree of polymerization (\bar{P}_n) equal to the reciprocal of the transfer constant. The reciprocals of the constants of Group 1 listed in Table III would give \bar{P}_n values of 1 to 7.

2. The polymerization of trinitroethyl methacrylate was carried out in bulk at 50°C, using various concentrations of catalyst (either methyl n-amyl ketone peroxide or 2,2'-azo-bis-isobutyronitrile). Table VI gives the variation of polymerization rate and intrinsic viscosity when various concentrations of the azonitrile initiator are used. Table VII gives similar data on the peroxide catalyst.

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TABLE VI

POLYMERIZATION OF TRINITROETHYL METHACRYLATE WITH
AZO bis-ISOBUTYRONITRILE AT 50°C

<u>Initiator Concentration mole/liter</u>	<u>Rate² (mole/liter/sec)²</u>	<u>Intrinsic Viscosity</u>
0	3.6×10^{-12}	0.064
0.00246	1.9×10^{-11}	0.061
0.00974	5.9×10^{-11}	0.062
0.0218	1.1×10^{-10}	0.061
0.0573	3.5×10^{-10}	0.070

TABLE VII

POLYMERIZATION OF TRINITROETHYL METHACRYLATE WITH
METHYL n-AMYL KETONE PEROXIDE AT 50°C

<u>Initiator Concentration mole/liter</u>	<u>Rate² (mole/liter/sec)²</u>	<u>Intrinsic Viscosity</u>
0	3.6×10^{-12}	0.065
0.00199	8.9×10^{-11}	0.067
0.00512	1.1×10^{-10}	0.070
0.0114	1.3×10^{-10}	0.058
0.0226	1.7×10^{-10}	0.071
0.0454	2.3×10^{-10}	0.058

Plotting the square of the rate (given in mole/liter/sec) against catalyst concentration (mole/liter) gives linear relationships. These are shown for the azonitrile in Figure 9 and for the ketone peroxide in Figure 10.

Variation of the Square of the Rate of Polymerization of
Trinitroethyl Methacrylate with Initiator Concentration

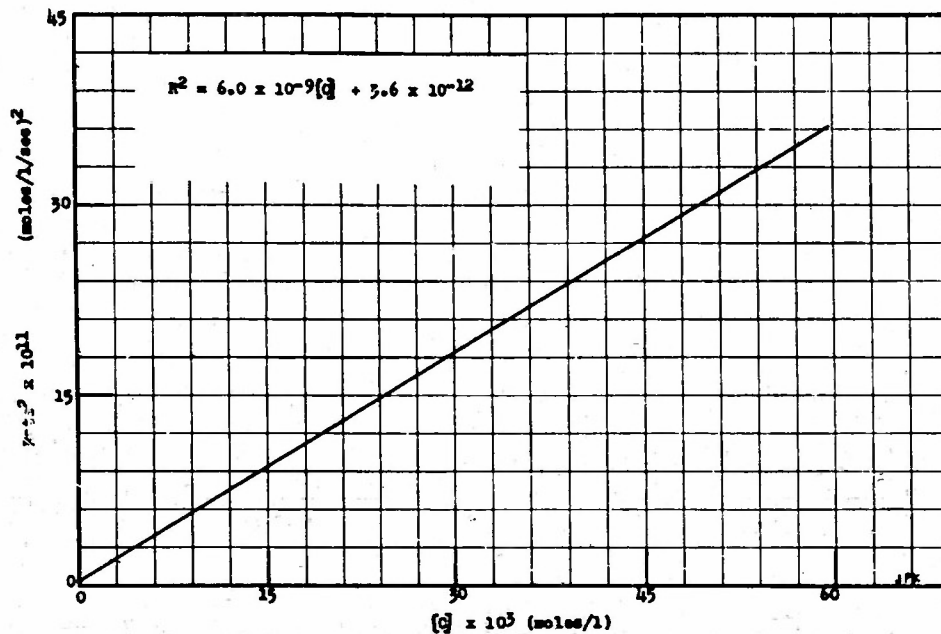


Figure 9

Variation of the Square of the Rate of Polymerization of Trinitroethyl
Methacrylate with Concentration of Methyl n-Amyl Ketone Peroxide

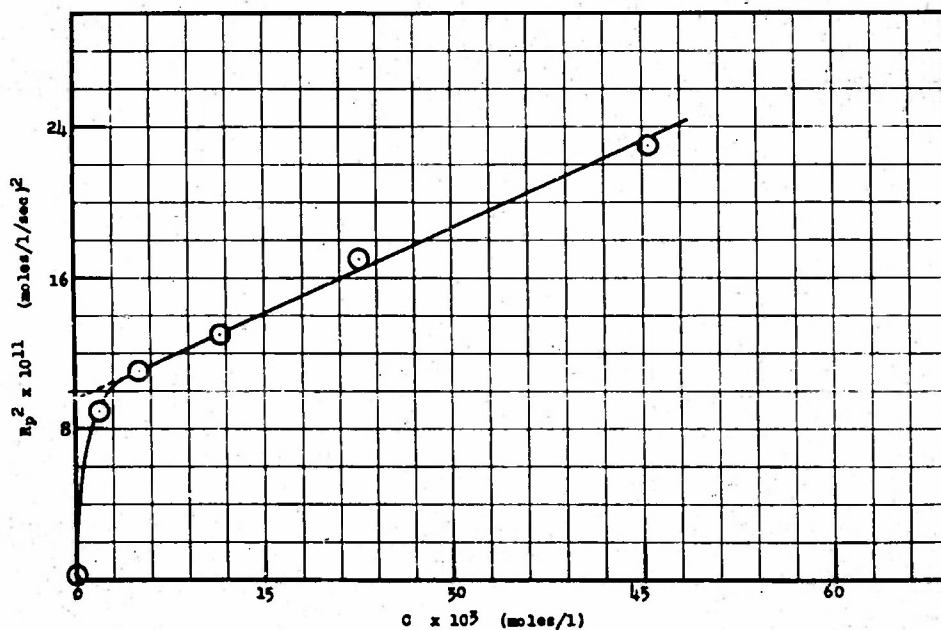


Figure 10

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The rates were determined from the initial slopes of the conversion curves shown in Figures 11 and 12.

Polymerisation of Trinitroethyl Methacrylate with Various Amounts of Azo-bis-isobutyronitrile

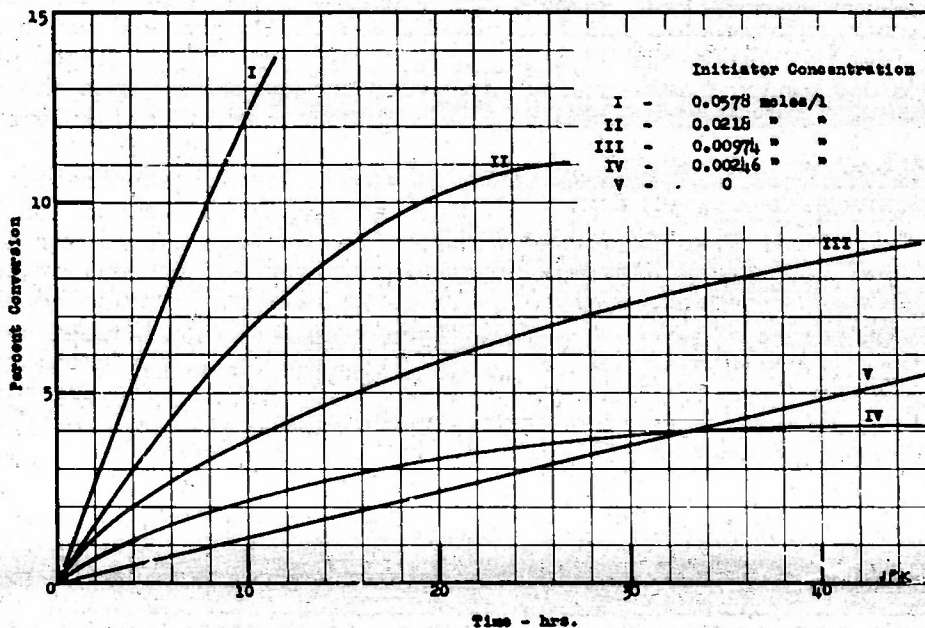


Figure 11

Polymerisation of Trinitroethyl Methacrylate with Various Amounts of Methyl n-Amyl Ketone Peroxide

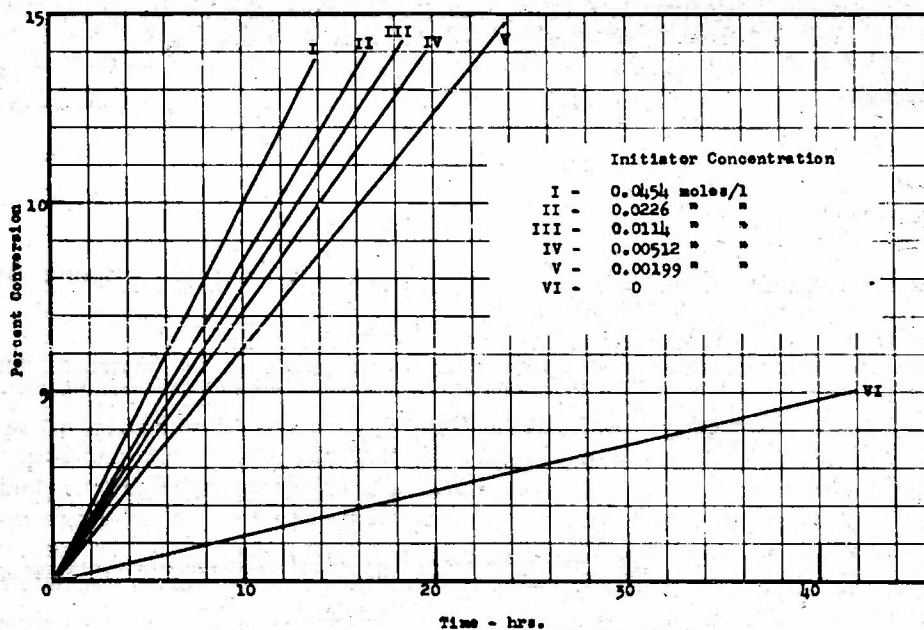


Figure 12

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3. It is noted in Figure 10 that methyl *n*-amyl ketone peroxide shows a linear relationship between the square of the rate and catalyst concentration. However, the line intersects the rate axis at a point considerably above the thermal rate. The difference between the observed thermal rate and the extrapolated linear relationship has been observed with styrene and benzoyl peroxide by Mayo et al. (Ref. 45). In the case of styrene only a slight deviation was noted and at appreciably lower initiator concentrations than those used here. Mayo attributed this difference to the fact that, in thermal polymerization, radicals are generated in pairs instead of in a statistical distribution throughout the reaction mixture. Inasmuch as there is a high local concentration of radicals, termination becomes easier. This increased rate of destruction of radicals should result in lower radical concentration and hence a slower polymerization rate. It must be pointed out that the effect observed is peculiar to the methyl *n*-amyl ketone peroxide. Inasmuch as little is known of the decomposition rate and other characteristics of this initiator it may be that induced decomposition is occurring. It is perhaps better to focus attention on the azonitrile catalyst, since it is known to decompose in a first-order, unimolecular manner in many organic solvents. Here a true linear dependence of the square of the rate with catalyst concentration is observed.

4. The thermal polymerization of trinitroethyl methacrylate was carried out in ethyl propionate solution at two different concentrations. The concentration, rate, and intrinsic-viscosity data are shown in Table VIII.

TABLE VIII

THERMAL POLYMERIZATION OF 2,2,2-TRINITROETHYL
METHACRYLATE IN ETHYL PROPIONATE AT 50°C

<u>Solvent/Monomer</u>	<u>Rate x 10⁷ moles/liter/sec</u>	<u>Intrinsic Viscosity</u>
0.5424	3.12	0.040
0.1057	14.3	0.054

Despite the admittedly meager data, it appears that the rate is proportional to the monomer concentration.

5. The intrinsic viscosities were calculated by means of the Baker-Philipoff equation from a single viscosity determination. For several samples the intrinsic viscosity was determined by plotting the ratio of specific viscosity to concentration against concentration of the polymer solution, and extrapolating to zero concentration. Excellent checks with the calculated values were obtained. It was also of interest to determine the number average molecular weight. The osmometric method of molecular-weight determinations is generally confined to polymers whose molecular weight exceeds 20,000. By means of special

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techniques reproducible results have been reported on polymer samples having molecular weights as low as 10,000. The osmometric molecular-weight determination of polytrinitroethyl methacrylate samples gave widely varying results. However, a successful method was established using the isopiestic cell for the molecular-weight determination (Ref. 46). With one polymer sample, experiments were conducted at nine different concentrations. The results are illustrated in Figure 13, which shows the variation of the reciprocal of molecular weight with polymer concentration at 25°C using acetone as solvent.

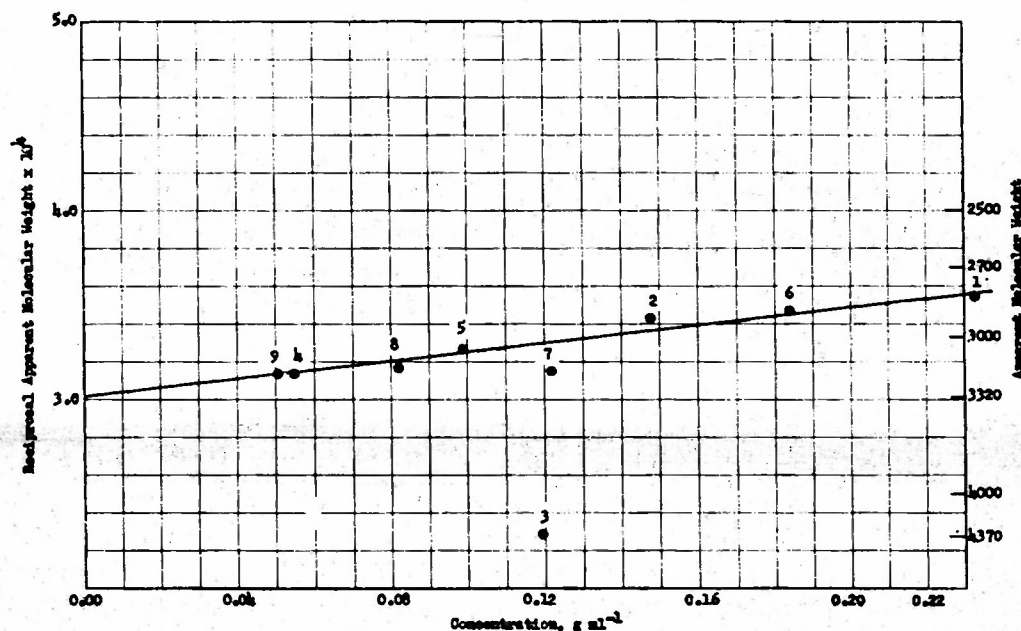


Figure 13

Poly-Trinitroethyl Methacrylate Molecular Weight Runs
Preparation JPK-30

6. The isopiestic molecular weight of 3320 is close to that which may be calculated from the analysis of the polymer. With the assumption that the polymer molecule consists of one-half the initiator molecule and thirteen monomer units, with the loss of one nitro group, good analytical agreement with the theoretical is observed.

Anal. of $C_{85}H_{105}N_{38}O_{105}$: %C, 30.57; %H, 3.17; %N, 15.93

Found: %C, 30.55; %H, 3.20; %N, 16.15

The molecular weight of this compound is 3339.

From the data which have been accumulated, an attempt may be made to account for the mechanism of the polymerization by kinetic analysis. The following discussion will present the kinetic derivations for two of the simplest mechanisms possible.

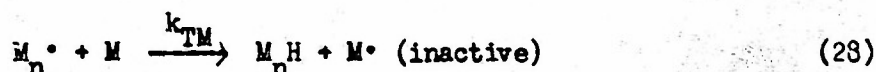
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8. Case I

Inasmuch as the molecular weight is extremely low it is assumed that all chains are terminated by a transfer reaction and that the transfer radical is incapable of chain initiation. The following series of reactions would be obtained:



At the steady-state concentration of radicals:

$$k_1 (\text{cat}) = k_{TM} (M_n\cdot) (M) \quad (29)$$

$$(M_n\cdot) = \frac{k_1 (\text{cat})}{k_{TM} (M)} \quad (30)$$

Because the rate of polymerization was determined by the rate of formation of polymer and not by the rate of monomer disappearance, the polymerization rate will be given by:

$$\frac{dP}{dt} = k_2 (M_n\cdot) (M) \quad (31)$$

Substitution of (30) into (31) yields:

$$\frac{dP}{dt} = \frac{k_1 k_2 (\text{cat})}{k_{TM}} \quad (32)$$

This indicates that the polymerization rate should be proportional to the first power of the catalyst concentration. The degree of polymerization (\bar{P}_n) would be given by:

$$\bar{P}_n = \frac{k_2}{k_{TM}} \quad (33)$$

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VI Discussion of Results, D (cont.)

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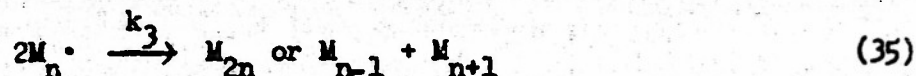
The reciprocal,

$$1/\bar{P}_n = \frac{k_{TM}}{k_2} \quad (34)$$

is the chain-transfer constant defined by Mayo. This mechanism thus accounts for constant chain length but differs from the data in that the rate is dependent upon the first power of the catalyst concentration and not the square root.

9. Case II

Here it is assumed that the transfer radical may initiate additional chains and that termination occurs by the mutual saturation of two polymer chains. In addition to Equations (26), (27), and (28), the following is needed:



At the steady state:

$$k_1 (\text{cat}) = k_3 (M_n \cdot)^2 \quad (36)$$

$$M_n \cdot = \left(\frac{k_1}{k_3} (\text{cat}) \right)^{1/2} \quad (37)$$

Again in this case the rate of polymerization is given by Equation (31):

$$\frac{dP}{dt} = k_2 (M_n \cdot) (M) \quad (31)$$

Substitution of (37) into (31) gives:

$$\frac{dP}{dt} = k_2 \left(\frac{k_1}{k_3} \right)^{1/2} (\text{cat})^{1/2} (M) \quad (38)$$

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For the degree of polymerization \bar{P}_n , one obtains

$$\bar{P}_n = \frac{k_2(M)}{k_3(M_n^\bullet) + k_{TM}(M)} \quad (39)$$

Substitution of (37) into (39) gives:

$$\bar{P}_n = \frac{k_2(M)}{(k_1 k_3)^{1/2} (cat)^{1/2} + k_{TM}(M)} \quad (40)$$

The data satisfy this mechanism with respect to the rate, which is proportional to the square root of the catalyst concentration, but not with respect to the dependence of the molecular weight upon catalyst concentration.

10. It is probable that the polymerization mechanism is quite complex and that a situation may exist which is analogous to that found by Burnett and Melville (Ref. 42) for the polymerization of vinyl acetate in benzene, toluene, and chlorobenzene. These investigators have shown by a rigorous kinetic analysis of the data that the transfer radical obtained from these solvents is somewhat stabilized. A time lag occurs between the cessation of one polymer chain and the initiation of another chain. The result is a retardation of the polymerization rate. In the case of trinitroethyl methacrylate it is possible that the transfer radical is also somewhat stabilized, resulting in a retarded rate. Another possibility that could exist would be the initiation of new chains by only a fraction of the stabilized transfer radicals. In either case it would be necessary to know the absolute values of the individual reaction coefficients before such an analysis could be made.

11. Although the exact mechanism for the polymerization of trinitroethyl methacrylate is unknown, the data which have been obtained are of value in providing a basis for the prediction of the behavior of analogous monomers. Heretofore, nothing was known about the polymerization of such monomers.

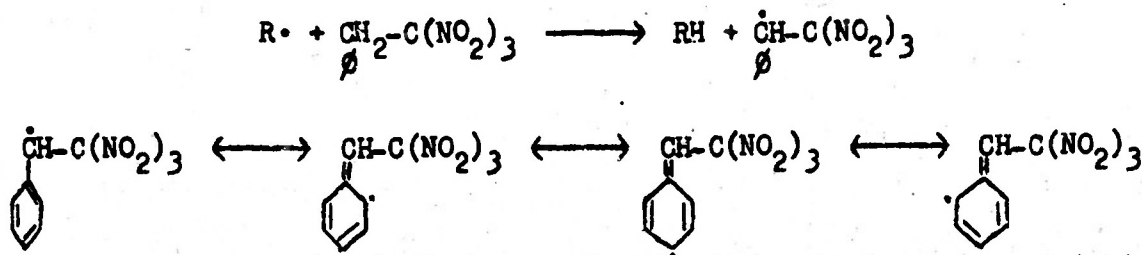
VII. RECOMMENDATIONS FOR FUTURE WORK

A. The need for a high-molecular-weight nitropolymer cannot be over-emphasized. In order to obtain a better understanding of nitro groups in polymer reactions the chain-transfer work should be expanded by the study of additional structures. The nitro compound 2-phenyl-1,1,1-trinitroethane would be of interest. If the theory of transfer by alpha-hydrogen abstraction is correct, the resulting radical, in this case, would have considerable resonance stability; i.e.,

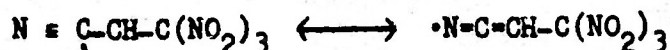
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VII Recommendations for Future Work, A (cont.)

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Likewise, the radical produced from 3,3,3-trinitropropionitrile would have stability due to resonance:



The possibility of allylic resonance in the 4,4,4-trinitro-1-butenyl radical would make this compound worth studying:



B. It would also be of interest to study the change of the chain-transfer constant with temperature. The activation energy for the transfer reaction could be calculated for nitro compounds of different structures. Any anomalous steric effects would then be evident.

C. In an effort to gain more information on the transfer reaction, it would be worthwhile to study the polymerization of methyl methacrylate in a high concentration of nitro solvent. Analysis of the resulting low-molecular-weight polymer should then give an indication of the number of nitro groups incorporated in the polymer. This in turn would give a clue to the type of transfer reaction occurring. This type of polymerization reaction, wherein the number of monomer units in the polymer is small, is known as telomerization. If such a reaction occurred very readily it might be of importance in the commercial production of special chemicals. A simple example would be the polymerization of ethylene in the presence of nitroform. If the reaction proceeded to give a terminal trinitromethyl compound, hydrolysis would give a series of fatty acids of various chain lengths.

D. The attempts to prove the alpha-hydrogen theory by dimerization of simple molecules by radicals should be carried out using acetyl peroxide. Its decomposition gives the methyl free radical, which is far more reactive than the tertiary radical produced from 2,2'-azo-bis-isobutyronitrile.

E. The use of the present condensation polymers in formulated compositions makes it important to study the chain-transfer effects of the various groups found in the polymers. For example, nothing is known of the urethane group in transfer reactions. The work might even be extended to non-nitro compounds which contain other active groups about which nothing is known. Examples are very active hydrogen compounds and as $\text{CH}_2(\text{CO}_2\text{R})_2$, $\text{CH}(\text{CO}_2\text{R})_3$, ureas, amines, $\phi_3\text{CH}$, $\phi\text{CH}_2\text{CO}_2\text{R}$, etc.

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